

## BACKGROUND OF THE INVENTION

## Field of the Invention

The present invention relates to a recording medium suitable for use in recording with inks and a production process thereof. In particular, the present invention relates to a recording medium for ink-jet, which can provide images high in optical density and bright in color tone, and has excellent ink-absorbing capacity, a production process thereof, and an image forming process using such a recording medium.

## Related Background Art

In recent years, an ink-jet recording system, in which minute droplets of an ink are ejected by any one of various working principles to apply them to a recording medium such as paper, thereby making a record of images, characters and/or the like, has been quickly spread as a recording apparatus for various images in various applications including information instruments because it has features that recording can be conducted at high speed and with a low noise, color images can be formed with ease, recording patterns are very flexible, and development and fixing process are unnecessary.

Further, it begins to be applied to a field of recording of full-color images because images formed by a multi- color ink-jet system are comparable in quality

# THE HISTORY OF THE

4B  
A2 ✓ 10

UB  
A3

with multi-color prints by a plate making system and  
photoprints by a color photographic system, and such  
printed images can be obtained at lower cost than the  
usual multi-color prints and photoprints when the  
number of copies is small.

With the improvement in recordability such as  
speeding up and high definition of recording, and full-  
coloring of images in the ink-jet recording system,  
recording apparatus and recording methods have been  
improved, and recording media have also been required  
to have higher properties. In order to satisfy such  
requirements, a wide variety of recording media have  
heretofore been proposed. For example, Japanese Patent  
Application Laid-Open No. 55-5830 discloses paper for  
ink-jet recording, in which a coating layer having good  
ink absorbency is provided on a surface of a substrate,  
and Japanese Patent Application Laid-Open No. 55-51583  
discloses that amorphous silica is used as a pigment in  
a coating layer.

Besides, recording sheets having an ink-receiving  
layer using an alumina hydrate of a pseudo-boehmite  
structure have been proposed in U.S. Patent Nos.  
4,879,166 and 5,104,730, and Japanese Patent  
Application Laid-Open Nos. 2-276670, 5-32413 and 5-  
32414.

Further, Japanese Patent Application Laid-Open  
No. 2-276670 discloses alumina sol which forms a

563  
R3  
CONFIDENTIAL

CONFIDENTIAL  
563  
R3

5

0

15

20

25

4B  
7A

543  
AS  
CUT

uniform orientation of the boehmite crystals has involved a problem that producing conditions are difficult to control.

2. Japanese Patent Application Laid-Open No.

5 7-76162 describes a recording medium in which a silica layer is laminated on a pseudo-boehmite layer. The idea described in the above document relates to the prevention of scratch marking by providing the silica layer. However, this method involves a problem that  
10 scratch marking is reduced, but blow marking cannot be prevented.

SUMMARY OF THE INVENTION

It is an object of the present invention to solve  
15 the above-described problems and to provide a recording medium which permits the choice of inks in a wide range, can provide images high in optical density, has good transparency and scarcely causes cracking, dusting and curling, a production process thereof, and an image  
20 forming process using such a recording medium.

The above object can be achieved by the present invention described below.

According to the present invention, there is thus provided a recording medium comprising a substrate and  
25 an ink-receiving layer provided on the substrate, wherein the ink-receiving layer comprises an alumina hydrate having a boehmite structure, an average

4wB  
A4

15

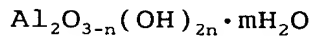
20

25

The alumina hydrate used in the present invention

is preferred as a material used in an ink-receiving layer because it has a positive charge, so that a dye in an ink is well fixed and an image good in coloring is hence provided, and moreover there are no problems of bronzing of a black ink and light fastness. The alumina hydrate used in the recording medium is preferably an alumina hydrate showing a boehmite structure when analyzed by the X-ray diffractiometry because it has good coloring material-adsorbing ability, ink absorbency and transparency.

The alumina hydrate is defined by the following general formula:



wherein n is an integer of 0 to 3, and m is a number of 0 to 10, preferably 0 to 5. In many cases,  $m\text{H}_2\text{O}$  represents an aqueous phase which does not participate in the formation of a crystal lattice, but is able to be eliminated. Therefore, m may take a value other than an integer. However, m and n are not 0 at the same time.

A crystal of the alumina hydrate showing a boehmite structure is generally a layer compound the (020) plane of which forms a macro-plane, and shows a characteristic diffraction peak. Besides perfect boehmite, a structure called pseudo-boehmite and containing excess water between layers of the (020) plane may be taken. The X-ray diffraction pattern of

44B  
A7

5

10

15

20

25

1. The first part of the document is a list of references. The references are listed in two columns. The first column contains references 1 through 10, and the second column contains references 11 through 20. The references are as follows:

1. The first part of the document is a list of references.	11. The first part of the document is a list of references.
2. The first part of the document is a list of references.	12. The first part of the document is a list of references.
3. The first part of the document is a list of references.	13. The first part of the document is a list of references.
4. The first part of the document is a list of references.	14. The first part of the document is a list of references.
5. The first part of the document is a list of references.	15. The first part of the document is a list of references.
6. The first part of the document is a list of references.	16. The first part of the document is a list of references.
7. The first part of the document is a list of references.	17. The first part of the document is a list of references.
8. The first part of the document is a list of references.	18. The first part of the document is a list of references.
9. The first part of the document is a list of references.	19. The first part of the document is a list of references.
10. The first part of the document is a list of references.	20. The first part of the document is a list of references.

4/18

[illegible]

No particular limitation is imposed on the production process of the ultrahigh orienting alumina hydrate used in the present invention so far as it is a process capable of producing an alumina hydrate having a boehmite structure. For example, the alumina hydrate can be produced by a method such as the hydrolysis of an aluminum alkoxide or sodium aluminate.



5

10

20

LuB  
Ag

54B  
A9  
Cont'd

aspect ratio) of the alumina hydrate can be determined by dispersing the alumina hydrate in ion-exchanged water, dropping the resultant dispersion on a collodion membrane to prepare a sample for measurement, and  
5 observing this sample through a transmission electron microscope.

According to a finding of the present inventors, the alumina hydrate in the flat plate form has better dispersibility in water than that of the needle form  
10 (ciliary form), and the orientation of particles of the alumina hydrate becomes random when an ink-receiving layer is formed therefrom, so that the pore volume of the ink-receiving layer increases, and the range of the pore radius distribution widens. Such an alumina  
15 hydrate is hence more preferred. The needle form as used herein refers to a state that molecules of an alumina hydrate in the form of a needle aggregate like a hair bundle with their sides in contact.

The most preferable shape of the alumina hydrate  
20 in the present invention is such that in the form of the flat plate, the average particle thickness is within a range of from 2.0 to 6.0 nm, and the average particle diameter is within a range of from 1 to 50 nm. In the case of the needle form on the other hand, it is  
25 preferred that the average particle diameter is within a range of from 2.0 to 6.0 nm, and the average particle length be within a range of from 1 to 50 nm. When the

average particle thickness or average particle diameter falls within the above range, the self-film-forming property and orienting ability of the alumina hydrate can be improved, so that the occurrence of coating defects, curling before printing and curling after printing in the resulting recording medium is prevented. The more preferable range of the average particle thickness or average particle diameter is a range of from 2.0 to 5.0 nm, since spaces are defined between particles of the alumina hydrate, and so the ink absorbency of the resulting ink-receiving layer can be improved. The most preferable range is a range of from 3.0 to 5.0 nm, within which a porous structure that the range of the pore radius distribution is wide can be formed with ease. Such an alumina hydrate can improve the transparency of the resulting ink-receiving layer and the coloring of images printed thereon.

The crystal structure of the alumina hydrate can be determined by general X-ray diffractometry. More specifically, the alumina hydrate, a recording medium provided with an ink-receiving layer containing this alumina hydrate, or a recording medium containing the alumina hydrate therein is set to a measuring cell to measure a peak which appears at a diffraction angle  $2\theta$  of 14 to 15°, whereby a crystallite size in a direction of a (020) plane (hereinafter referred to "crystallite size") can be found in accordance with the Scherrer's

formula

$$E = 0.9\lambda/B\cos\theta \quad [1]$$

wherein  $\lambda$  is a wavelength of an X-ray,  $2\theta$  is a diffraction angle at the peak, and B is a half breadth of the peak.

In the present invention, the crystallite size is within a range of from 5.0 to 8.0 nm. When the crystallite size falls within this range, the transparency of the resulting recording medium can be improved without impairing the self-film-forming property of the alumina hydrate.

The crystallite size is preferably greater than the average particle thickness or average particle diameter, since the occurrence of bleeding and cissing can be prevented. More preferably, a difference between the crystallite size and the average particle thickness or average particle diameter is at least 1 nm. When the difference satisfies this limitation, the resulting recording medium becomes hard to undergo dusting and cracking when it is folded. The most preferable difference between the crystallite size and the average particle thickness or average particle diameter is at least 2 nm. When the difference satisfies this limitation, the occurrence of beading and whitish haze on an image printed on the resulting recording medium can be prevented.

The term "bleeding" as used herein means that

56B  
A10

56B  
A11

when solid printing is conducted at a fixed area on a recording medium, a portion colored with a dye becomes wider (greater) than a printed area. The term "beading" means a phenomenon that a particulate concentration irregularity appears due to aggregation of ink droplets caused at a solid printed area. The term "cissing" means that portions not colored occur in a solid printed area. The term "whitish haze" means that an image printed looks whitely hazy.

The degree of parallelization in the recording medium according to the present invention is within a range of 30 to 1,000. When the degree of parallelization falls within this range, the occurrence of coating defects, curling before printing and curling after printing in the recording medium is prevented. The degree of parallelization is more preferably within a range of 50 to 800, since blow marks are hard to be left on the ink-receiving layer, and the coloring ability of the ink-receiving layer is improved to make a color at a color-mixed area, such as a secondary color, good. In the present invention, the degree of parallelization is determined by subjecting a recording medium and powder thereof to X-ray diffraction to find their respective peaks at a (020) plane and another plane, separately finding an intensity ratio between 2 peaks on both samples and comparing these intensity ratios with each other. No limitation is imposed on

54B  
N11  
CONTN

66220" 6940400  
54B  
N12

5 the reference peak so far as it has so sufficient intensity that it is not hidden by the peak of the base, like a combined peak of a (200) plane and a (051) plane, or a peak at a (120) plane. The above combined peak is preferred.

10 In another embodiment of the recording medium according to the present invention, an additional porous layer may be formed on the porous layer comprising the ultrahigh orienting alumina hydrate and a binder. Any material may be used for the upper layer so far as it is a material capable of forming a porous layer. For example, the material can be chosen for use from the group consisting of magnesia, magnesium carbonate, calcium carbonate, silica and silica-  
15 alumina. Of these, silica is most preferred. When a porous layer containing silica is provided as the upper layer, the ink-receiving layer becomes hard to leave scuff marks on the surface thereof, and moreover the ink-absorbing speed of the ink-receiving layer is  
20 increased. As the silica, may be used any of silica sol (colloidal silica) in which primary particles are monodispersed, colloidal particles of silica composed of secondary particles obtained by aggregating primary particles, gel type silica, and precipitated silica.  
25 Either dry process or wet process may be used as the production process of the silica. The shape of the silica used may be either, for example, spherical or

non-spherical. No particular limitation is imposed on the particle diameter of the silica. However, it is preferably within a range of from 3 to 200 nm. When the particle diameter falls within this range, the ink absorbency and transparency of the resulting recording medium can be reconciled with each other. Two or more kinds of silica may also be used in combination. In this case, a combination of the inorganic fine particles having a particle diameter of 20 nm or smaller and a particle diameter within a range of from 40 to 200 nm is desirable from the viewpoints of the prevention of cracking and good transparency. As described in Japanese Patent Application Laid-Open No. 6-183131, silica having a particle diameter of 20 nm or smaller may also be used as a binder. The particle diameter of the silica is more preferably 100 nm or smaller because no surface disorder occur after printing, and the roundness of printed dots is made better.

The BET specific surface area, pore radius distribution and pore volume of the ink-receiving layer of the recording medium according to the present invention can be determined by the nitrogen adsorption and desorption method. The BET specific surface area is preferably within a range of from 70 to 300 m<sup>2</sup>/g. If the BET specific surface area is smaller than the lower limit of the above range, the resulting ink-receiving

66260-63740  
SUB  
P/B  
CONT

SUB  
P/B  
25

layer becomes opaque white, or its adsorption sites to a dye in an ink becomes insufficient, so that the water fastness of an image printed thereon may become insufficient in some cases. If the BET specific surface area is greater than the upper limit of the above range, the resulting ink-receiving layer becomes easy to cause cracking. The ink-receiving layer preferably has a structure that a maximum peak in the pore radius distribution (peak pore radius) thereof is present within a range of from 5.0 to 10.0 nm in radius. When the peak is present within this range, the transparency and ink absorbency of the resulting recording medium can be improved. A more preferred range in radius is a range of from 5.0 to 8.0 nm. When the peak is present within this range, the resolution of an image to be formed on the resulting ink-receiving layer is improved, and the tint of a black ink is kept constant irrespective of concentration. Further, the total pore volume of the ink-receiving layer is preferably within a range of from 0.35 to 1.0 cm<sup>3</sup>/g, more preferably from 0.4 to 1.0 cm<sup>3</sup>/g because ink absorbency is improved irrespective of the kind of ink. A still more preferred range is a range of from 0.4 to 0.6 cm<sup>3</sup>/g. When the total pore volume falls within this range, the tint at a color-mixed area in an image formed is improved. The pore volume of the ink-receiving layer is preferably at least 8 cm<sup>3</sup>/m<sup>2</sup>. If the

543  
DPA  
cut 12

662605460



543  
Any  
cut

pore volume is smaller than this limit, inks tend to run out of the ink-receiving layer when multi-color printing is conducted, and so bleeding occurs on an image formed.

5        The pore structure and the like of the ink-receiving layer are not determined only by the alumina hydrate used, but changed by various production conditions such as the kind and mixing amount of the binder, the concentration, viscosity and dispersion  
10       state of the coating formulation, coating equipment, coating head, coating weight, and the flow rate, temperature and blowing direction of drying air. It is therefore necessary to control the production  
15       conditions within the optimum limits for achieving the intended properties of the ink-receiving layer according to the present invention. In the present invention, a slurry of the alumina hydrate is mixed  
20       with a binder without drying the slurry to powder, and the resultant mixture is applied to a substrate, thereby producing a recording medium.

As the binder used in the present invention, one or more materials may be freely chosen for use from among water-soluble polymers. For example, preference may be given to polyvinyl alcohol or modified products  
25       thereof, starch or modified products thereof, gelatin or modified products thereof, casein or modified products thereof, gum arabic, cellulose derivatives

such as carboxymethyl cellulose, polyvinyl pyrrolidone, maleic anhydride polymers or copolymers thereof, water-soluble polymers such as acrylic ester copolymers, conjugated diene copolymer latexes such as SBR latexes, functional group-modified polymer latexes, vinyl copolymer latexes such as ethylene-vinyl acetate copolymers, and the like.

The mixing ratio by weight of the alumina hydrate to the binder is preferably within a range of from 5:1 to 20:1. When the mixing ratio falls within this range, the ink-absorbing speed of the resulting recording medium is increased, and the optical density of an image printed thereon can be heightened. If the amount of the binder is less than the lower limit of the above range, the mechanical strength of the resulting ink-receiving layer becomes insufficient, and the ink-receiving layer tends to cause cracking and dusting. If the amount is greater than the upper limit of the above range, the pore volume of the resulting ink-receiving layer is reduced, resulting in a printing medium having poor ink absorbency. The mixing ratio is more preferably within a range of from 7:1 to 15:1 taking into consideration the points that ink absorbency is improved, and cracking is hard to occur when the resulting recording medium is folded.

In the present invention, pigment dispersants, thickeners, pH adjustors, lubricants, flowability

modifiers, surfactants, antifoaming agents, water-proofing agents, foam suppressors, releasing agents, foaming agents, penetrants, coloring dyes, optical whitening agents, ultraviolet absorbents, antioxidants, antiseptics and mildewproofing agents may be added in addition to the alumina hydrate and binder, as needed. The water-proofing agents may be freely chosen for use from among the known substances such as quaternary ammonium halides and quaternary ammonium salt polymers.

No particular limitation is imposed on the substrate used for forming the ink-receiving layer thereon so far as it is a sheet-like substance, for example, a paper web such as suitably sized paper, water leaf paper or resin-coated paper making use of polyethylene or the like, or a thermoplastic film. In the case of the thermoplastic film, there may be used transparent films such as films of polyester, polystyrene, polyvinyl chloride, polymethyl methacrylate, cellulose acetate, polyethylene and polycarbonate, as well as opaque sheets opacified by the filling of a pigment or the formation of minute foams.

As a process of the dispersion treatment for a dispersion containing the alumina hydrate, any process may be chosen for use from among the processes generally used in dispersion. As a method and apparatus to be used, mild stirring by a homomixer,

rotary blade or the like is preferred to stirring by a grinder type dispersing machine such as a ball mill or sand mill.

Although shearing stress applied varies according to the viscosity, amount and volume of the dispersion, it is preferably within a range of from 0.1 to 100.0 N/m<sup>2</sup> (1 to 1,000 dyn/cm<sup>2</sup>). When the shearing stress falls within the above range, the viscosity of the alumina hydrate dispersion can be reduced without changing the crystal structure of the alumina hydrate. In addition, the particle diameter of the alumina hydrate can be made sufficiently small, so that binding points between the alumina hydrate, and the binder, substrate and fibrous substance are increased. Therefore, the occurrence of cracking and dusting can be prevented. If the shearing stress exceeds the upper limit of the above range, the dispersion undergoes gelation, or the crystal structure of the alumina hydrate is changed to an amorphous form. If the shearing stress is lower than the lower limit of the above range, dispersion becomes insufficient, so that the resulting dispersion tends to generate precipitate, aggregated particles are left in the resulting recording medium to cause haze, thereby lowering the transparency of the recording medium, and the recording medium tends to cause separation of the particles and cracking.

SECRET

5413  
Dy

Shearing stress ranging from 0.1 to 50.0 N/m<sup>2</sup> is more preferred because the pore volume of the alumina hydrate is not decreased, and more over aggregated particles of the alumina hydrate can be broken into fine particles, so that the formation of pores having a greater radius in the resulting recording medium can be prevented to prevent separation and cracking of the ink-receiving layer when the recording medium is folded, and the occurrence of haze due to great particles in the recording medium can be reduced.

Shearing stress ranging from 0.1 to 20.0 N/m<sup>2</sup> is most preferred because the mixing ratio of the alumina hydrate to the binder in the resulting recording medium can be kept constant to prevent the occurrence of dusting and cracking, and moreover the optical density and dot diameter of dots printed on the recording medium can be made even.

Although the dispersing time varies according to the amount of the dispersion, the size of a container, the temperature of the dispersion, and the like, it is preferably 30 hours or shorter from the viewpoint of preventing the change of the crystal structure. When the dispersing time is 10 hours or shorter, the pore structure can be kept within the above ranges. During the dispersion treatment, the temperature of the dispersion may be kept constant by conducting cooling or heat retaining. Although a preferable temperature

sub  
A17

66260"6940460

range varies according to the process of the dispersion treatment, and materials and viscosity of the dispersion, it is within a range of from 10 to 100°C.

If the temperature is lower than the lower limit of the  
5 above range, the dispersion treatment becomes  
insufficient, or aggregation occurs. If the  
temperature is higher than the upper limit of the above  
range, the dispersion undergoes gelation, or the  
crystal structure is changed to an amorphous form.

10 In the present invention, as a coating process of  
the dispersion comprising the alumina hydrate in the  
case where an ink-receiving layer is formed, there may  
be used a generally-used coating technique using a  
blade coater, air knife coater, roll coater, brush  
15 coater, curtain coater, bar coater, gravure coater,  
sprayer or the like.

The coating weight of the dispersion is preferably within a range of from 0.5 to 60 g/m<sup>2</sup> in terms of dry solids content from the viewpoint of good ink absorbency. The coating weight is more preferably within a range of from 5 to 45 g/m<sup>2</sup>. When the coating weight falls within this range, the ink-absorbing speed of the resulting recording medium is increased, and the cracking and curling of the recording medium can be prevented. The surface smoothness of the ink-receiving layer may also be improved by means of calender rolls or the like as needed.

[illegible]

25

25

as methyl alcohol; amides such as dimethylformamide;  
ketones and keto-alcohols such as acetone; ethers such  
as tetrahydrofuran; polyalkylene glycols such as  
polyethylene glycol; alkylene glycols the alkylene  
5 moiety of which has 2 to 6 carbon atoms, such as  
ethylene glycol; glycerol; lower alkyl ethers of  
polyhydric alcohols, such as ethylene glycol methyl  
ether; and the like. Among these many water-soluble  
organic solvents, the polyhydric alcohols such as  
10 diethylene glycol, and the lower alkyl ethers of  
polyhydric alcohol, such as triethylene glycol  
monomethyl ether and triethylene glycol monoethyl ether  
are preferred. The polyhydric alcohols are  
particularly preferred because they have an effect as a  
15 lubricant for preventing the clogging of nozzles, which  
is caused by the evaporation of water in an ink and  
hence the deposition of a water-soluble dye.

A solubilizer may be added to the inks.  
Nitrogen-containing heterocyclic ketones are typical  
20 solubilizers. Its object is to highly enhance the  
solubility of the water-soluble dye in the solvent.  
For example, N-methyl-2-pyrrolidone and 1,3-dimethyl-2-  
imidazolidinone are preferably used. In order to  
further improve the properties of inks, additives such  
25 as viscosity modifiers, surfactants, surface tension  
modifiers, pH adjustors and resistivity regulative  
agents may be added.



[illegible]
$$\frac{1}{A^2} \frac{1}{B}$$

20

25

- An alumina hydrate slurry or an ink-receiving

layer containing an alumina hydrate separated from a recording medium sample was dispersed in ion-exchanged water, and the resultant dispersion was dropped on a collodion membrane to prepare a sample for measurement.

5 This sample was observed through a transmission type electron microscope (H-500, trade name, manufactured by Hitachi Ltd.) to find an average particle thickness or average particle diameter.

2. Crystallite size (nm):

10 Powder obtained by drying an alumina hydrate slurry at 100°C for 8 hours, or powder of an ink-receiving layer separated from a recording medium sample was thoroughly ground in an agate mortar to prepare a powder sample. The sample was placed on a  
15 sample carrier to subject it to X-ray diffractometer (RAD-2R, trade name, manufactured by RIGAKU CORPORATION), thereby finding a half breadth at a (020) plane. The crystallite size was determined in accordance with the Scherrer's formula.

20 3. Self-film-forming property of alumina hydrate slurry:

An alumina hydrate slurry was applied to a transparent PET film (Melinex 705, trade name, product of Du Pont Co.) having a thickness of 100  $\mu\text{m}$  by a die  
25 coating process so as to give a dry coating thickness of 10  $\mu\text{m}$  and then dried at 100°C for 20 minutes. The coating surface was visually observed to evaluate the

alumina hydrate slurry as to the self-film-forming property in accordance with the following standard:

AA: None of coating defects were observed, and a fine continuous film was formed;

5           A: Cracks 5 mm or smaller in length were present, but a comparatively good continuous film was formed;

B: Cracks greater than 5 mm in length were present, but a continuous film was formed;

10           C: Cracks were continuous, and no continuous film was formed.

4. Degree of parallelization of recording medium:

15           With respect to a recording medium sample, peak intensity of a (020) plane and combined peak intensity of (051) and (200) planes in X-ray diffraction were measured. An ink-receiving layer separated from the recording medium was thoroughly ground in an agate mortar to prepare a powder sample. The combined peak intensity of this powder sample was measured likewise.

20           The degree of parallelization was determined from these measured results in accordance with the following formulae.

Intensity ratio of powder =

25           ( Peak intensity of the (020) plane of the powder ) /  
             ( Combined peak intensity of the (051) and (200)  
             planes of the powder )

Intensity ratio of recording medium (sheet form) =

(Peak intensity of the (020) plane of the medium)/  
(Combined peak intensity of the (051) and (200)  
planes of the medium)

Degree of parallelization =

5 (Intensity ratio of the recording medium (ink-  
receiving layer))/((Intensity ratio of the powder).

5. Pore volume and peak pore radius of recording  
medium:

After a recording medium sample was thoroughly  
10 heated and deaerated, measurement was conducted using  
the nitrogen adsorption and desorption method.

Measuring apparatus: Autosorb 1 (trade name,  
manufactured by Quantachrome  
Co.).

15 6. Ink absorbency:

Using an ink-jet printer equipped with four ink-  
jet heads for yellow (Y), magenta (M), cyan (C) and  
black (Bk) inks, each of which has 128 nozzles at  
intervals of 16 nozzles per mm, ink-jet recording was  
20 performed on a recording medium sample in an ink  
quantity of 30 ng per dot with inks having their  
corresponding compositions described below, thereby  
evaluating the recording medium as to ink absorbency.

Ink composition

25	•Ink dyes (Y, M, C and Bk)	5 parts each
	•Ethylene glycol	9 parts
	•Polyethylene glycol	11 parts

•Water

75 parts

Ink dyes

Y: C.I. direct yellow 86

M: C.I. acid red 35

5 C: C.I. direct blue 199

Bk: C.I. food black 2

Using the yellow, magenta, cyan and black inks, single-color or multi-color solid printing was conducted on the recording medium. Right after the printing, the drying condition of the inks on the surface of the recording medium was determined by touching the printed area with a finger. The quantity of each ink in the single-color printing was determined as 100 % (16 x 16 dots per mm<sup>2</sup>). Similarly, overlap printing was performed with 3 color inks (each 100 %). The ink absorbency was ranked in accordance with the following standard.

- AA: No ink adhered to the finger in an ink quantity of 300 %;
- 20 A: No ink adhered to the finger in an ink quantity of 200 %;
- B: No ink adhered to the finger in an ink quantity of 100 %;
- C: Some ink adhered to the finger in an ink quantity of 100 %.
- 25

7. Transparency of recording medium:

The total light transmittance of each recording

medium produced was measured by means of a hazeometer (NDH-1001DP, trade name, manufactured by Nippon Denshoku K.K.) in accordance with JIS K-7105. The transparency was ranked in accordance with the following standard.

AA: Transmittance of at least 75 %;

A: Transmittance of at least 70 %;

B: Transmittance of at least 60 %;

C: Transmittance lower than 60 %;

8. Resistance to curling after printing of recording medium:

Each recording medium produced was cut into a size of 297 by 210 mm, and solid printing was conducted in an ink quantity of 300 % in the same manner as in the evaluation of ink absorbcency with 20-mm blank spaces left at all peripheral sides of the recording medium. The recording medium thus printed was placed on a flat table with the ink-receiving layer turned upward to measure the height of warpage by a height gage. The resistance to curling of the recording medium was ranked in accordance with the following standard.

AA: Warpage was not more than 0.2 mm;

A: Warpage was not more than 1 mm;

B: Warpage was not more than 5 mm;

C: Warpage was more than 5 mm.

9. Coating defects of recording medium:

66666-634066

343  
A22

5

A: Cracks not longer than 1 mm occurred in a proportion of at most 5 cracks per 297 x 210 mm;

10

10. Resistance to curling before printing of recording medium (curling of blank sheet):

15

C: Warpage was more than 1 mm.

Each recording medium produced was brought into close contact with a glass plate with the ink-receiving

layer turned upward, and a pencil (Uni Series, trade name, product of Mitsubishi Pencil Co., Ltd.) rounded off at one end thereof was dropped on the recording medium from a height of 20 cm with the rounded end turned downward. Whether some blow mark was left on the recording medium or not at this time was visually observed to rank the resistance to blow marking in accordance with the following standard.

AA: No blow mark was observed;

10 A: A blow mark not greater than 1 mm in diameter was observed;

B: A blow mark not greater than 2 mm in diameter was observed;

15 C: A blow mark greater than 2 mm in diameter was observed.

12. Folding test:

Each recording medium produced was wound in close contact around a column 10 mm in diameter with the ink-receiving layer outside and folded at an angle of 180°. The condition of the ink-receiving layer at this time was visually observed to evaluate it in accordance with the following standard.

AA: No change was observed;

25 A: A crack not longer than 3 mm was observed in parallel with the fold curve;

B: A crack not shorter than 3 mm was observed in parallel with the fold curve, but no



separation of the ink-receiving layer from the substrate (PET) was observed;

C: Separation of the ink-receiving layer from the substrate (PET), which was attendant on a crack caused in parallel with the fold curve, was observed.

EXAMPLE 1:

Aluminum sec-butoxide was prepared in accordance with the process described in U.S. Patent No. 4,242,271. A mixed solution of the aluminum sec-butoxide and 75 % by weight sec-butyl alcohol was hydrolyzed at 85°C with a mixed solution of sec-butyl alcohol containing 30 % by weight of water at a velocity gradient of 5,000 cm<sup>-1</sup> in a vessel equipped with a stirrer to prepare an alumina hydrate slurry. After this alumina hydrate slurry was aged at 125°C for 3 hours in an electromagnetic stirring type autoclave, water was immediately added to the alumina hydrate slurry until the solids content of alumina hydrate was 20 % by weight, to cool it. The pH of the alumina hydrate slurry was adjusted with a 3.8 % aqueous nitric acid solution to obtain a slurry of an alumina hydrate having a boehmite structure. The physical property values of the thus-obtained slurry of the alumina hydrate having the boehmite structure were determined in accordance with the above-described respective methods. The results are shown in Table 1.

Polyvinyl alcohol (Gohsenol GH23, trade name, product of The Nippon Synthetic Chemical Industry Co., Ltd.) was dissolved or dispersed in ion-exchanged water to obtain a 10 % by weight solution. The polyvinyl alcohol solution and the alumina hydrate slurry obtained by the above-described process were weighed out so as to give a weight ratio of 1:15 in terms of solids content and mixed with each other while stirring for 30 minutes at 8,000 rpm by means of a homomixer (manufactured by Tokushu Kika Kogyo Co., Ltd.), thereby obtaining a mixed dispersion. The mixed dispersion was applied by a die coating process onto a transparent PET film (Lumirror, trade name, product of Toray Industries, Inc.) having a thickness of 100  $\mu\text{m}$ . The PET film on which the mixed dispersion had been coated was placed into an oven (manufactured by YAMATO SCIENTIFIC CO., LTD.) to heat and dry it at 100°C for 30 minutes, thereby obtaining a recording medium in which an ink-receiving layer having a thickness of 39  $\mu\text{m}$  was formed. The physical property values of the ink-receiving layer were determined in accordance with the above-described respective methods. The results are shown in Table 1.

EXAMPLES 2 to 7:

Slurries of alumina hydrates having a boehmite structure were obtained in the same manner as in Example 1 except that the temperature and stirring

velocity (velocity gradient) upon the hydrolysis, the temperature and time upon the aging, and the quenching operation with diluent ion-exchanged water (when no quenching was conducted, the slurry was allowed to cool down to room temperature after the aging and then diluted) in Example 1 were changed to their corresponding conditions shown in Table 1. The physical property values of the respective alumina hydrate slurries thus obtained were determined in accordance with the above-described respective methods. The results are shown in Table 1. Recording media, in which an ink-receiving layer was formed, were obtained in the same manner as in Example 1 except that these alumina hydrate slurries were respectively used. The physical property values of the respective ink-receiving layers were determined in accordance with the above-described respective methods. The results are shown in Table 1.

EXAMPLES 8 and 9:

Alumina hydrate slurries were obtained in the same manner as in Example 1 except that  $\text{Na}_2\text{SiO}_3$  was added as a shape-controlling agent to the alumina hydrate slurry prepared in Example 1 in such a manner that the weight ratio of the alumina hydrate slurry to  $\text{Na}_2\text{SiO}_3$  was 10:0.05 in terms of solids content, and the aging time was changed as shown in Table 1. The physical property values of the respective alumina

hydrate slurries thus obtained were determined in accordance with the above-described respective methods. The results are shown in Table 1. Recording media, in which an ink-receiving layer was formed, were obtained in the same manner as in Example 1 except that these alumina hydrate slurries were respectively used. The physical property values of the respective ink-receiving layers were determined in accordance with the above-described respective methods. The results are shown in Table 1.

#### COMPARATIVE EXAMPLES 1 and 2:

Slurries of alumina hydrates having a boehmite structure were obtained in the same manner as in Example 1 except that the stirring velocity (velocity gradient) upon the hydrolysis, the temperature and time upon the aging, and the quenching operation with diluent ion-exchanged water (when no quenching was conducted, the slurry was allowed to cool down to room temperature after the aging and then diluted) in Example 1 were changed to their corresponding conditions shown in Table 1. The physical property values of the respective alumina hydrate slurries thus obtained were determined in accordance with the above-described respective methods. The results are shown in Table 1. Recording media, in which an ink-receiving layer was formed, were obtained in the same manner as in Example 1 except that these alumina hydrate slurries

were respectively used. The physical property values of the respective ink-receiving layers were determined in accordance with the above-described respective methods. The results are shown in Table 1.

5 COMPARATIVE EXAMPLE 3:

An alumina hydrate slurry was obtained in the same manner as in Example 8 except that  $\text{Na}_2\text{SiO}_3$  was added as a shape-controlling agent to the alumina hydrate slurry prepared in Example 1 in such a manner  
10 that the weight ratio of the alumina hydrate slurry to  $\text{Na}_2\text{SiO}_3$  was 10:0.05 in terms of solids content. The physical property values of the alumina hydrate slurry thus obtained were determined in accordance with the above-described respective methods. The results are  
15 shown in Table 1. A recording medium, in which an ink-receiving layer was formed, was obtained in the same manner as in Example 1 except that this alumina hydrate slurry was used. The physical property values of the ink-receiving layer were determined in accordance with  
20 the above-described respective methods. The results are shown in Table 1.

COMPARATIVE EXAMPLE 4:

A slurry of an alumina hydrate having a boehmite structure was obtained in the same manner as in Example  
25 1 except that the mixed solution of sec-butyl alcohol containing 30 % by weight of water used in the hydrolysis was changed to ion-exchanged water. The

physical property values of the alumina hydrate slurry thus obtained were determined in accordance with the above-described respective methods. The results are shown in Table 1. A recording medium, in which an ink-receiving layer was formed, was obtained in the same manner as in Example 1 except that this alumina hydrate slurry was used. The physical property values of the ink-receiving layer were determined in accordance with the above-described respective methods. The results are shown in Table 1.

Table 1

	Example							
	1	2	3	4	5	6	7	8
(Conditions of synthesis)								
Hydrolyzing temperature (°C)	85	85	85	85	85	90	80	85
Velocity gradient (cm <sup>-1</sup> )	5000	5000	1000	5000	5000	5000	5000	5000
Aging temperature (°C)	125	60	60	125	135	125	125	125
Aging time	3 hrs	5 days	24 hrs	5 hrs	6 hrs	2 hrs	1 hr	3 hrs
Quenching	Carried out	Not	Not	Carried out	Carried out	Carried out	Carried out	Carried out
(Physical properties of slurry)								
Average particle thickness (nm)	4.5	5	2	5	6	4.2	3	4.2
Crystallite size (nm)	5.5	5.2	2	6.4	8	5.2	5	5.6
Average particle diameter (nm)	21.1	20.3	16.5	22.5	23.2	28	19.5	22.8
Self-film-forming property	AA	A	B	AA	A	AA	AA	AA

Table 1 (continued)

	Example							
	1	2	3	4	5	6	7	8
(Physical properties of recording medium)								
Average particle thickness (nm)	4.5	5	2	5	6	4.2	3	4.2
Crystallite size (nm)	5.5	5.2	2	6.4	8	5.2	5	5.6
Degree of parallelization	500	100	30	450	50	700	850	800
Pore volume (cc/g)	0.51	0.52	0.34	0.6	0.7	0.4	0.36	0.53
Peak pore radius (nm)	6.7	6.8	4.2	8.5	10	4.9	4.6	6.9
Ink absorbency	AA	AA	B	AA	AA	A	A	AA
Transparency	A	A	AA	A	B	AA	AA	AA
Resistance to curling after printing	AA	A	B	AA	A	AA	AA	AA
Coating defects (cracking)	AA	A	A	AA	A	AA	AA	AA
Resistance to curling before printing	A	A	A	A	A	A	A	A
Resistance to blow marking	AA	A	B	AA	B	AA	AA	AA
Folding test	AA	A	B	AA	B	AA	AA	AA



Table 1 (continued)

	Example	Comparative Example			
		1	2	3	4
	9				
(Conditions of synthesis)					
Hydrolyzing temperature (°C)	85	85	85	85	85
Velocity gradient (cm <sup>-1</sup> )	5000	1000	5000	5000	5000
Aging temperature (°C)	125	60	125	125	125
Aging time	1 hr	5 days	3 hrs	0.5 hrs	3 hrs
Quenching	Carried out	Not	Not	Carried out	Carried out
(Physical properties of slurry)					
Average particle thickness (nm)	2	5.2	5.4	1.9	7
Crystallite size (nm)	5	5.2	5.2	4.2	6.9
Average particle diameter (nm)	19.4	20.9	23.2	19.5	29.2
Self-film-forming property	AA	C	C	AA	C

Table 1 (continued)

	Example	Comparative Example			
		1	2	3	4
(Physical properties of recording medium)					
Average particle thickness (nm)	2	5.2	5.4	1.9	7
Crystallite size (nm)	5	5.2	5.2	4.2	6.9
Degree of parallelization	1000	20	7	1500	5
Pore volume (cc/g)	0.35	0.45	0.45	0.35	0.6
Peak pore radius (nm)	4.5	6	5.8	4.5	8.5
Ink absorbency	A	A	A	B	AA
Transparency	AA	A	A	AA	A
Resistance to curling after printing	AA	C	C	AA	C
Coating defects (cracking)	AA	C	C	AA	C
Resistance to curling before printing	B	A	A	C	A
Resistance to blow marking	AA	C	C	AA	C
Folding test	AA	C	C	AA	C

EXAMPLE 10:

An aqueous dispersion containing polyvinyl alcohol (GH-23, trade name, product of The Nippon Synthetic Chemical Industry Co., Ltd.) at a solids concentration of 10 % by weight and colloidal silica (Snowtex OL, trade name, product of Nissan Chemical Industries, Ltd.) were mixed with each other so as to give a mixing ratio of 1:3 in terms of solids content, and the resultant mixture was stirred for 5 minutes at 2,000 rpm by means of a homomixer (manufactured by Tokushu Kika Kogyo Co., Ltd.). The mixed dispersion was applied onto the ink-receiving layer of the recording medium produced in Example 1 and dried to form a porous silica layer having a thickness of 10  $\mu$ m. The resultant recording medium was evaluated in the same manner as in Examples 1 to 9. As a result, the transparency, resistance to curling before printing, resistance to curling after printing and the like remained unchanged. Further, tack and scuff marks did not occur.

EXAMPLE 11:

Colloidal silica (Snowtex YL, trade name, product of Nissan Chemical Industries, Ltd.) and ultrafine particulate colloidal silica (Snowtex UP, trade name, product of Nissan Chemical Industries, Ltd.) as a binder were mixed with each other so as to give a mixing ratio of 1:1 in terms of solids content, and the

resultant mixture was subjected to a dispersion treatment in the same manner as in Example 1, thereby obtaining a dispersion. This dispersion was applied onto the ink- receiving layer of the recording medium produced in Example 1 in the same manner as in Example 10 and dried to form a silica layer having a thickness of 10  $\mu$ m. The resultant recording medium was evaluated in the same manner as in Examples 1 and 10. As a result, the same results as in Example 10 were obtained.

EXAMPLE 12:

Gel type silica (P-78A, trade name, product of Mizusawa Industrial Chemicals, Ltd.) was dispersed in ion-exchanged water to obtain a dispersion at a solids concentration of 10 % by weight. This dispersion and the same polyvinyl alcohol dispersion as that used in Example 1 were mixed at a mixing ratio of 3:1 in terms of solids content, and the resultant mixture was subjected to a dispersion treatment in the same manner as in Example 1, thereby obtaining a mixed dispersion. This dispersion was applied onto the ink-receiving layer of the recording medium produced in Example 1 in the same manner as in Example 10 and dried to form a silica layer having a thickness of 10  $\mu$ m. The resultant recording medium was evaluated in the same manner as in Examples 1 and 10. As a result, the same results as in Example 10 were obtained.

The present invention has the following marked effects.

1. Since the ultrahigh orienting alumina hydrate according to the present invention has a boehmite structure, the recording media according to the present invention can provide printed image excellent in resolution, coloring and tinting, and moreover are excellent in transparency.

2. Since the ultrahigh orienting alumina hydrate according to the present invention has self-film-forming property, there can be provided recording media which scarcely cause curling before printing, curling after printing and environmental curing. In addition, the occurrence of coating defects in an ink-receiving layer can be prevented. Further, coating speed can be increased because the coating formulation containing such an alumina hydrate sets, so that productivity can be improved.

3. Blow marking, cracking by folding, and dusting are hard to occur. Even when the ink-receiving layer is marred, the marred portion thereof becomes hard to be separated.